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CHAS. J. J. FOX

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PART II: CARBONIC ACID

WITH 5 FIGURES

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ON THE COEFFICIENTS OF ABSORPTION OF THE ATMOSPHERIC GASES IN DISTILLED WATER AND SEA WATER

BY

CHAS. J. J. FOX

PART II: Carbonic Acid.

In considering the conditions according to which the Carbonic Acid of the Atmosphere dissolves and is found contained in sea water, it has to be borne in mind, in the first place, that the amount dissolved is dependent not only upon the Pressure, Temperature and Salinity (chlorine concentration) as in the case of the other chief atmospheric Gases, Nitrogen and Oxygen, but is influenced also by an additional independent variable, the Alkalinity; the effect of which is due to a chemical as distinct from a purely physical influence.

In addition to determinations of Salinity and Temperature, it is therefore required to know for each observation, the pressure of the CO_2, (which is very much smaller than that of atmospheric Oxygen and Nitrogen of course), the Alkalinity and the total quantity of CO_2. In the experiments which are here to be described, these determinations were made as follows.

The Chlorine was determined by titration with Silver Nitrate solution, using Potassium Chromate as indicator in the usual way.

The Alkalinity was determined by first adding to a known quantity of sea-water (250—500 cc. usually) a quantity of standardized acid, 0.1 Normal, from a Knudsen's pipette which is very convenient and accurate for the purpose; and by then heating the whole until all CO_2 had been expelled and titrating hot the excess of acid, by means of Barium Hydroxide with Phenolphthalein as indicator. The heating may be done by boiling gently over a naked flame in an open evaporating basin for 10—15 minutes. But a Jena flask is perhaps safer and was nearly always used; though experiments carried out specially for the purpose showed that there is very little if any chance at all, of losing any HCl even by violent heating, and this in spite of the 2 % or so of Cl present in sea water.

In Oceanography it has been usual to determine the excess of acid by adding Potassium Iodate and then titrating the Iodine set

free by means of Sodium Thiosulphate solution. A series of direct experiments of comparison, however, made it clear that the iodometric method has for the present purpose no advantage over the direct titration against $Ba(OH)_2$. And moreover it was found that in using the iodometric method it is very easy to get too high results; in every case it is essential that the solution be quite cold before the Iodate be added, otherwise Iodine will be lost and the Alkalinity of the sea water will come out too high. Titration with $Ba(OH)_2$ and Phenolphthalein is certainly less inconvenient and more certain than the Iodometric method, in the present case. For this reason the Alkalinity determinations of the present work were always done by this method.

The total quantity of Carbonic Acid dissolved, was determined by means of the apparatus which the writer has previously described[1]). About 300 cc. of the sea-water was allowed to enter the evacuated flask-receiver (through tube *a*, Fig. 1 *loc. cit.*) where it was heated with a measured quantity of standard acid, introduced from a Knudsen's pipette and the Carbonic Acid pumped off and measured gasometrically in the usual way. With the help of a filter pump the sea-water together with the excess of acid was thereupon removed from the flask (through *a* again) into another one for titration with $Ba(OH)_2$. In this way the total Carbonic Acid and Alkalinity were determined in one operation upon the same quantity of sea water[2]).

Since the description of this apparatus was first published it has been improved in one or two small details (Fig. 1). The neck of the flask is now enlarged above the rubber stopper to take a mercury sealing; the limb of the double T-piece upon which the rubber stopper is borne, is made very slightly conical and rather longer than it was made formerly; so that it may be made to give a very tight join without trouble either in getting the flask on or off. It is better to have the piece of glass-tubing which dips to the bottom of the flask, replaced by rubber tubing instead of glass; which being hard is dangerous to the flask when in violent ebulition, it hits against the latter.

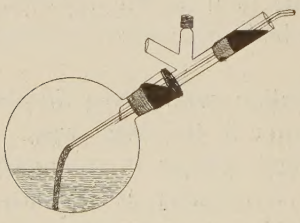

Fig. 1.

The platinum points too, sealed into the Burette of this apparatus, by means of which the mixture of gases is exploded for the determination of Oxygen, now pass through small glass tubes sealed to the Burette and terminated above in small cups containing mercury; which serve to connect with Battery and Coil for sparking[3]). It should have been pointed out in

[1]) Publications de circonstance No. 21, Copenhague 1905.

[2]) Thus it is possible to determine N_2, O_2, CO_2 and Alkalinity upon one and the same sample of Sea-water and in one operation. If necessary the Chlorine too could be determined, with an accuracy quite sufficient for the present purpose, by making certain obvious corrections.

[3]) Illustrated in Ostwald-Luther: Phys. Chem. Messungen 2te Aufgabe (Fig. 69).

the published description cited, that the quantity of Hydrogen and Oxygen exploded together should be kept always low compared with the quantity of Nitrogen present; otherwise some of the Nitrogen may be lost to the analysis by the formation of Nitrous Acid[1]). There is no difficulty in this, once recognised, because the amount of Hydrogen sufficient to wash out the last traces of gas is very small indeed and may easily be kept down to 2—5 cc.; then the explosion is never very violent and the consequent risk of losing Nitrogen is small. It is also preferable perhaps, to lubricate the burette taps with Phosphoric Pentoxide instead of grease; owing to the grave errors that may be produced by the possible combustion of fats in the explosions.

Several methods of determining the CO_2-pressure in the air were tried, and the one which as a result seemed to be the most adaptable to the purposes of the present work, and was therefore used in the case of all the measurements here included, was PETTENKOFER's slightly modified. One of the possible causes of serious inaccuracy in this method is the action of Alkali upon the glass bottle. In the present instance preliminary experiments were made with a constant quantity of $Ba(OH)_2$ solution in which several bottles were used, varying in size between 20 litres and 8 litres; one of more or less new white glass, one very old white glass bottle, one old green glass bottle, which had on a former occasion been kept for many weeks filled with hot water, and two bottles made of Jena Geräte glass. It was found that the bottle of new white glass was suspicious; the others gave very concordant results, with certain precautions which seemed obvious. The Jena Geräte glass bottles were used for practically all the measurements.

The determination of CO_2 in the air was made as follows. A large bottle of known capacity, filled with tap water, having been emptied in the place from which the air sample was desired, and closed with a rubber stopper, a known quantity of Standard Baryta solution was added to the bottled air. After the CO_2 had been absorbed and precipitated as $BaCO_3$, the excess of $Ba(OH)_2$ was determined by titration against standard Succinic Acid, with Phenolphthalein as indicator. Rosolic Acid is used by many workers, as indicator. This titration gives the data necessary for the calculation of the amount of CO_2. The analysis should be done twice on two samples of air collected simultaneously in two different sized bottles.

If sea-water has been shaken in the bottle and it is desired to know how much CO_2 still remains in the air left within, after the shaking, it is necessary first to get the sea-water out of the bottle, then to add the standard $Ba(OH)_2$ solution and to titrate as before. But in this case a

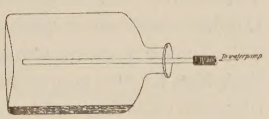

Fig. 2.

[1]) This observation is due originally to BUNSEN. See *e. g.* TRAVERS Experimentelle Untersuchung von Gasen. Braunschweig 1905. p. 94.

difficulty arises owing to the presence of a trace of $NaCl$ from the sea-water being left behind, hanging to the walls of the bottle, which reacts with precipitated $BaCO_3$ to form soluble Sodium Carbonate; this spoils the end point in the titration. The trouble is got over by adding some strong $BaCl_2$ or $Ba(NO_3)_2$ solution, so that the ionic concentration of $Ba^{\bullet\bullet}$ may be always very great compared with that of the small quantity of $Na^{\bullet}$; the point of neutrality is then sufficiently sharp and easily to be determined, with Succinic Acid and Phenolphthalein.[1])

[1]) It is regrettable that the Ionic Theory has not yet been adopted as the basis for classifying Oceanographic results. KRÜMMEL in his Handbuch which for many years to come must be the standard treatise on Oceanography, has unfortunately classified and recalculated practically the whole of the material used, upon the arbitrary and irrational basis known as Salinity (Knudsen) instead of adopting the absolute and rational units of Cl $^0/_{00}$ and Sp. Gr. Salinity had been defined before in several arbitrary ways prior to Knudsen's now universally adopted unit; and it is presumably open to anyone to redefine salinity in any way which improved methods of chemical analysis may from time to time seem to suggest. For instance, in the work upon which Knudsen's Tables are founded, it was found impossible to get constant weight by evaporating the water and igniting the residual salts. This is without question due to the hydrolysis of Mg and Ca double chlorides with ensuing production (and loss!) of HCl and the formation of Hydroxides or Oxides, upon ignition; a fact long well known. If the residual salts had been ignited instead in an atmosphere of HCl, no doubt a constant weight would have been obtainable. All Carbonates and Hydroxides would have been quantitatively transformed into Chlorides; and after prolonged heating at very high temperatures possibly also the Bromides and Iodides too. In this way it would be possible to get a more precise unit of Salinity; but still only an arbitrary and irrational unit even then. The Chlorine per mille and Specific Gravity units are on the other hand absolute and rational; and it is to be deplored that Oceanographers still almost invariably use the salinity unit in preference to Cl $^0/_{00}$ and σ.

It is also unwarrantable and opposed to the facts, to describe salts (such as $NaCl$, KCl, $MgSO_4$ etc.) as existing dissolved in sea-water. The Ionic Theory makes it clear that in reality the positive ions $Na^{\bullet}$ $K^{\bullet}$ $Ca^{\bullet\bullet}$ $Mg^{\bullet\bullet}$ etc. must be in simultaneous equilibrium with each and all of the negative ions Cl' (Br' I') SO_4'', HCO_3' etc.; all analyses of sea-water should therefore be stated in terms of these ionic concentrations and not classified as $NaCl$, $MgSO_4$ etc.

The writer has had several requests to give an account of the Ionic Theory here; but exigences of space and the fact that every modern elementary text book does so more amply, makes this course undesirable. For this reason the Ionic Theory — and Guldberg and Waage's Law of Mass Action — have been assumed here, rather than explained. For the rest, reference may be made to ABEGG Die Theorie der Elektrolytischen Dissociation Stuttgart 1903 or LEHFELDT Electrochemistry London 1904 which give an ample and elementary exposition of these principles.

In the present work, following the customary notation, it may be explained that $Na^{\bullet}$, $K^{\bullet}$ etc. represent Sodium, Potassium (monovalent) kations and $Ca^{\bullet\bullet}$ $Mg^{\bullet\bullet}$ (divalent) Calcium and Magnesium kations; similarly Cl' SO_4'' and HCO_3' represent anions (monovalent, divalent or otherwise as the case may be). Concentrations are denoted by enclosing in brackets; thus $(H^{\bullet}) \times (OH') =$ Constant, indicates that the product of the concentrations of H ions and OH ions is constant.

In practice a measured quantity of one half to one litre of water was put into a large bottle (12 litres) of known capacity; which was then rotated about its axis placed horizontally in a framework designed for the purpose, driven by a small water-motor.[1]) With this arrangment agitation is very complete and the water soon comes into equilibrium with the air above it in the bottle; a thin film of water is carried round by the walls of the bottle in its rotation and is constantly renewed. If now a current of air from the outside be drawn through the bottle during the rotation, by means of a water pump (Fig. 2) the water soon comes into equilibrium with the atmosphere and with its CO_2; provided of course, that it is to begin with, not very much over — or under — saturated. The Atmosphere contains so little CO_2 that it is clear that if the water is very much over — or under — saturated to begin with, very large quantities of air will have to be drawn through before equilibrium can be attained. It is therefore convenient to agitate the sample, before putting into the bottle, with several large quantities of air, until it is approximately in equilibrium with the atmosphere; then to finish, as described, in the bottle. The air remaining in the bottle at the end is also analysed.

But it is required to make observations with samples of sea water, saturated with CO_2 also at pressures differing from the prevailing CO_2-partial pressures of the Atmosphere. It is then necessary that the bottle be closed and that after the rotation is complete the air inside, above the water, be analysed. In this case the bottle is closed with a stopper (Fig. 3) having two holes, one of which carries a straight piece of glass tube into the bottle; both holes are then closed with two additional small rubber stoppers. After rotation a piece of fairly thick rubber tubing closed with a clip, is pushed into the free hole of the stopper; the small rubber stopper being removed quickly for the purpose. Then the bottle having been placed vertically stopper-end down, the water can be run out for determination of its CO_2-contents and Alkalinity, its own volume of air at the same time flowing in through the glass tube to take its place; to admit which the other small stopper must be removed momentarily, and for which a small correction may be applied in the calculation of the subsequent analysis of the air within. This operation can be done quite easily and the water all drawn off, without agitation or aeration; a trace of sea-water always remains behind of course, hanging to the walls of the bottle which, as already noted, makes it necessary to add $BaCl_2$ solution before titrating the excess of $Ba(OH)_2$. The water having been run out for analysis, a known quantity of $Ba(OH)_2$

[1]) Jacobsen has already used the method in his determination of the solubility of Oxygen in Sea-Water. Meddelelser fra Kommissionen for Havundersøgelser. Serie: Hydrografi Bind 1 No 7, Kopenhagen 1905.

solution is added to the bottle from a Knudsen's pipette, and agitated until the CO_2 is all absorbed. Then $BaCl_2$ solution is added together with Phenolphthalein and the excess of $Ba(OH)_2$ titrated (while still in the bottle; at all events until very near the end point) with 0.05 normal Succinic Acid. For titration in this way it is convenient to have the outlet of the Burette below the tap, very much longer (5—6 times) than is usual.

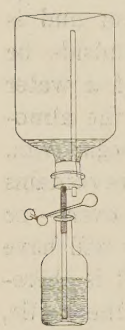

Fig. 3.

It is clear that the experiment as carried out in this way, has to be done at air temperature; and therefore to obtain a complete series between about 0° and 30°, it is necessary to work at different seasons of the year. It is also important that ventilation and air circulation be very complete and in direct communication with the free atmosphere: the work must be done in the shade too. In the case of the observations which will here be described attention was paid to all these points and satisfactory conditions of working were obtained; many series of observations were made in addition, which for one reason or another were thought to be not so reliable and were therefore rejected,

The Temperature was determined by having a thermometer hanging free in the air, one inside the bottle during rotation and one for taking the temperature of the water sample accurately, as it was drawn out of the bottle. The experiment was not regarded as quite satisfactory if these thermometers showed any persistent differences of more than about one or two tenths; usually the differences were much less,

As regards the water samples used, they were prepared from water taken from the open sea; water of Cl = 20 ‰ was obtained by evaporating slightly. In the work it was necessary to have samples of sea-water of any alkalinity and any quantity of CO_2, at will. This was provided for as follows.

A large quantity (about 30 litres) of water of Cl = 20 ‰ was prepared by evaporating ordinary sea-water. Its alkalinity was then determined upon several quantities of 500 cc. each, with the highest possible accuracy; then the quantity of acid (a mixture of HCl and H_2SO_4 in the exact ratio in which Cl : SO_4 is found in sea-water) required to just neutralize the whole of the remainder was added and most of the CO_2 got out of the sea-water by warming and diminishing the pressure with a filter pump.

From this stock solution and distilled water other stock solutions were prepared of about Cl = 0, 7.0, 14.0 and 20.0 ‰; each one of the four of course having zero alkalinity. Then about 3 litres of each of these four stock solutions was treated with CO_2 for some time (from a Kipp's apparatus) until it contained about 300—500 cc. CO_2 ‰.

It was kept in a well stoppered flask and a quantity analysed so that it was known about how much CO_2 it contained. Then by adding measured quantities of it, with a pipette, to known quantities of its original stock solution, it was possible to get at once samples of the solution containing approximately any desired amount of CO_2 at will; and to do this without altering the salinity or adding to the Alkalinity.

A modification of this arrangment made it possible to alter the Alkalinity at will, without altering the salinity. For this purpose the smaller stock solutions, again about 3 litres, each had dissolved in it a small amount of CO_2 and some pure Na_2CO_3; it was then shaken vigorously with air and its total CO_2 and Alkalinity determined. Then by adding small measured quantities of it to known quantities of its original stock solution it was possible to vary the Alkalinity at will without altering the Salinity and at the same time to obtain at once a solution which was not very much over or under saturated with CO_2 and therefore not far from equilibrium with the atmosphere.

To vary the CO_2 at will without varying the Alkalinity or Salinity, a quantity of pure $NaHCO_3$ was dissolved in the 3 litres, while to the original stock solution the exact equivalent quantity of pure NaOH was added. This latter quantity was determined by titration.

These quantities of salts are so small that they are quite without influence upon the other properties of the sea-water itself; the effect produced is for instance not sufficient to disturb the ratio of Na : Cl : SO_4 : Specific Gravity, by any appreciable quantity. The quantities here concerned are only milligrams per litre. The theoretical sanction for these arrangments will be given below; and it is believed the results will be found to confirm the assumptions which led to their adoption.

As is well known CO_2 on dissolving in distilled water follows Henry's Law very closely; at all events up to 2—3 atmospheres pressure. Some other "soluble" gases (*e. g.* H_2S, NH_3 and SO_2) also follow Henry's Law between fairly wide limits; whilst others again (*e. g.* HCl) show marked divergence from it. Following Henry's Law is only consonant with the gas having the same molecular weight in both the gaseous and liquid phases; and the only compound of water and CO_2 known is H_2O,CO_2 or H_2CO_3.[1]) It is known that this substance is an extremely weak acid with an ionisation relation at 25° given by[2])

$$(H\bullet) \times (HCO_3') = 3 \times 10^{-7}(H_2CO_3)$$

That is to say, of the amount of H_2CO_3 present only 3×10^{-7} of it is ionised in the first stage of ionisation. The second dissociation

[1]) V'ant Hoff Vorlesungen über theoretische u. physikalische Chemie Heft II S. 20 Braunschweig 1899.

[2]) Walker and Cormack Journal of Chemical Society 778 (1900).

represented by $HCO_3' \rightarrow H^{\bullet} + CO_3''$, as is usual with all dibasic acids, is very much smaller (20000 times) than the first dissociation[1]) and is for the purposes of the present work of no account; as will be shown.

CO_2 also dissolves in neutral salt solution (*e. g.* NaCl aq.) according to Henry's Law[2]); at the samé time the solubility is diminished by the salt, owing to the physical effect of its presence upon water as a solvent, at a rate proportional over considerable limits, to the concentration of the salt. The solubility of CO_2 in water and NaCl solutions has been very accurately determined by Bohr[3]) from whose observations Table 1 has been compiled in the form most useful for present purposes. It gives for varying temperatures and varying concentrations of Cl ‰ the no. of cc. of CO_2 which would be dissolved bv 1000 cc. of neutral solution from a free atmosphere containing one part of CO_2 gas per 10000.

Table 1

t	Cl=0	Cl=2	Cl=4	Cl=6	Cl=8	Cl=10	Cl=12	Cl=14	Cl=16	Cl=18	Cl=20
− 2	0.1943	0.1817	0.1791	0.1765	0,1739	0.1713	0.1687	0.1661	0.1635	0.1609	0.1583
0	0.1713	0.1690	0.1667	0.1644	0.1621	0.1598	0.1575	0.1552	0.1529	0.1506	0.1483
2	0.1583	0.1563	0.1543	0.1523	0.1503	0.1483	0.1463	0.1443	0.1423	0.1403	0.1383
4	0.1473	0.1453	0.1423	0.1403	0.1383	0.1363	0.1343	0.1323	0.1303	0.1283	0.1263
6	0.1377	0.1360	0.1343	0.1326	0.1309	0.1292	0.1275	0.1258	0.1241	0.1224	0.1207
8	0 1283	0.1263	0.1243	0.1223	0.1203	0.1183	0.1163	0.1143	0.1123	0.1103	0.1083
10	0 1193	0.1177	0.1161	0.1145	0.1129	0.1113	0.1097	0.1081	0.1065	0.1049	0.1033
12	0.1117	0.1103	0.1089	0.1075	0.1061	0.1047	0.1033	0.1019	0.1005	0.0991	0.0977
14	0.1050	0.1037	0.1024	0.1011	0.0998	0.0985	0.0972	0.0959	0 0946	0.0933	0.0920
16	0.0987	0.0973	0.0959	0.0945	0.0931	0.0917	0.0903	0.0889	0.0875	0.0861	0.0847
18	0.0927	0.0917	0.0907	0.0897	0.0887	0.0877	0.0867	0.0857	0.0847	0.0837	0.0827
20	0.0877	0.0867	0.0857	0.0847	0.0837	0.0827	0.0817	0.0807	0.0797	0.0787	0.0777
22	0.0830	0.0820	0.0810	0.0800	0.0790	0.0780	0.0770	0.0760	0.0750	0.0740	0 0730
24	0.0780	0.0773	0.0766	0 0759	0.0752	0.0745	0.0738	0.0731	0.0724	0.0717	0.0710
26	0.0737	0.0730	0 0723	0.0716	0 0708	0.0702	0.0695	0.0688	0.0681	0.0674	0.0667
28	0.0700	0.0690	0.0680	0.0670	0.0660	0.0650	0.0640	0.0630	0.0620	0.0610	0.0600
30	0.0667	0.0657	0.0647	0.0637	0.0627	0.0617	0.0607	0.0597	0.0587	0.0577	0.0567

If instead of a partial pressure of CO_2 of 1 ‰ some other proportion (*e. g.* 3 ‰, as is usually found in the atmosphere) is contained in the gas phase, then the no. of cc of CO_2 dissolved in the liquid phase which will be in equilibrium with it, is obtained simply

[1]) Bodländer Zeit. für Phys. Chem. XXXV 23 1900.

[2]) Setschenow Bulletin de la Societé Imperiale des Naturalistes de Moscou 1, 2, 3 (1905).

[3]) Bohr Ann. des Physik u. Chemie 62 (1897) 614.

by multiplying the amount found from the table for 1 ‰ by the new pressure (in the case of the atmosphere this factor is of course usually about 3). Thus at 10° a solution of 6 ‰ Cl dissolves 0.114 cc of CO_2 per litre from an atmosphere containing 1 ‰ CO_2 or $3 \times 0.114 = 0.342$ cc CO_2 from an atmosphere containing 3 ‰ CO_2.

It is seen that the amount of CO_2 which would be dissolved by the open Ocean if it were perfectly neutral, from the open atmosphere (CO_2 = 3 ‰) would be very small and would never be more than 0.48 cc ‰ for Cl = 20 ‰ and 0.57 for Cl = 0 ‰ [1]). But it is known that sea-water commonly contains up to as much as 120 times these small quantities; that is 60 cc or even more per litre. And the difference between this latter quantity and the ½ cc or so which would otherwise be present, were the sea-water quite neutral, is kept in solution in equilibrium with the 3 ‰ CO_2 of the atmosphere, by the presence of the excess of Base over Acid which is always found in sea-water analyses [2]).

This was first established clearly by Tornöe and by Dittmar. At the same time these investigators also introduced, as it would seem unfortunately, a cryptic method of expressing this Alkalinity as they termed it, which has persisted down to the present day. According to their definition, Alkalinity is the quantity of CO_2 required by the excess of base over acid found in 1000 cc of sea-water, to convert it into Normal Carbonate: or in other words one half of the quantity which would be necessary to convert it into Bicarbonate. This quantity of CO_2 is now invariably expressed in cc; it was formerly also expressed sometimes in mgms.

The sanction for this arbitrary definition was derived from the fact that solid Carbonates and Bicarbonates are well defined bodies of known composition, obtainable by the direct action of CO_2 upon the caustic alkalies. And it was assumed that the excess of base in the sea-water, in solution that is, reacted with CO_2 also in two stages to form first Carbonate and then with more CO_2 to form Bicarbonate. The latter stage in the sea is hardly more than commenced; or as Dittmar put it, the CO_2 in sea-water is more than sufficient to complete the formation of the Carbonate but considerably less than is required to form the Bicarbonate. And in this way the practice has grown up and is even now followed, of referring to Carbonates and Bicarbonates as present in sea-water; of classifying results and of expressing all sorts of hypothetical equilibrium relations in terms of Carbonates and Bicarbonates. The process according to this view is represented in its two stages by the following equations (R represents as usual, a monovalent Basic radical)

$$2\ ROH + CO_2 = R_2CO_3 + H_2O$$
$$H_2O + R_2CO_3 + CO_2 = 2\ RHCO_3$$

The constitution of substances in the solid state in reality however,

[1]) See Krümmel Handbuch der Ozeanographie, Stuttgart 1903 S. 293.

[2]) That is to say, when the CO_2 is left out of account in these analyses.

does not necessarily afford any indication of what takes place when the same substances are dissolved. Such a view leaves out of account altogether, the possibility of reaction between the dissolved substance and the solvent. And in the present case the fallacious analogy has served only to confuse the issue.

When a normal Carbonate R_2CO_3 dissolves in water a definite quantity of it ionizes; and since it is the salt of a divalent weak acid — that is an acid the ionisation constant of which is not of very different magnitude to that of pure water — reaction with the water takes place, until a state of equilibrium is reached. The Carbonate is said to be hydrolized and the equilibrium relation expressing it is

$$R_2CO_3 + HOH \rightleftarrows 2\ R\bullet + HCO_3' + OH';$$

the solution reacts alkaline, as is well known, owing to the formation of Hydroxyl (OH′) ions in excess of the OH′ concentration of pure water.

In this case, if an atmosphere containing CO_2 were to be brought into contact with this solution, a definite quantity of CO_2 would enter it; some H•-ions would be produced and reaction with the excess of OH′-ions would ensue, to produce water

$$\left.\begin{aligned} CO_2 + H_2O &\rightleftarrows H\bullet + HCO_3' \qquad (a) \\ OH' + H\bullet + HCO_3' &\rightleftarrows H_2O + HCO_3' \quad (b) \end{aligned}\right\}$$

until a state of equilibrium would be reached; in other words a stage where no more CO_2 either enters or leaves the solution. At this point, if it were found that there had been altogether just enough CO_2 to provide just the amount of H•-ions (according to *a*) necessary to react with just all the excess of OH′, with production of water, then it is clear that no more free CO_2 would be left over, either in the atmosphere above or in the water; the CO_2 would have been all transformed into HCO_3' and no excess of H• ions would be left in the solution. The solution would then be neutral; it would contain H• and OH′ in concentrations equal to one another and the same as for pure water; for the rest the solution would of course contain also R• ions. If instead of just enough CO_2 there were insufficient to "neutralize" all the excess of OH, then it is clear that after having absorbed the whole of the CO_2 (and transformed it into HCO_3') the solution would continue to react alkaline, though now more weakly than before, and would retain its power, now somewhat weakened, of reacting with additional CO_2 should it at any time have the opportunity. If however there be rather more than sufficient CO_2 to neutralize the OH′, then a quantity of CO_2 must go on entering the solution after neutrality has been attained, with production of H• ions and an acid reaction.

But though the concentration of OH′ which is found in solution at the end, may be either equal to, greater than or less than tbe concentration of H• ions present alongside of it, accordiug to the proportional amounts of each available for reaction, yet whatever the proportion, the product of the two concentrations of H• and OH′ remains constant for all proportions and equal to that of the water in which the reaction takes place. This is required by and is the direct consequence of GULDBERG and WAAGE's Law of Mass Action.

In Nature it is always found that the Atmosphere contains CO_2 in constant quantity approximating to 3 $^0/_{000}$, even above the Ocean; and this

means that there must be more CO_2 available than is required to neutralise the excess OH' of sea-water. If CO_2 be not in excess, then it would still go on entering the sea-water from the Atmosphere and eventually, if sufficient were not available to neutralize all the residual OH' of the Ocean, all CO_2 would disappear from the Atmosphere and the Ocean would remain capable of absorbing still more if only more were available. The CO_2 of the Atmosphere is no doubt, like water vapour, always quite or very nearly in equilibrium with the Ocean; should it at any moment be not in equilibrium then CO_2-evolution or dissolution, as the case may be, must tend soon to restore equilibrium. The Ocean therefore as a whole is in equilibrium with an excess of CO_2 in the Atmosphere of about 3 $^0/_{000}$; and there is thus a corresponding small residual $H\bullet$-concentration (acidity) due to the small amount of $CO_2 H_2O$ in the solution, which is in equilibrium with the CO_2 of the Atmosphere and is in excess of what is requisite for just neutralizing the Alkalinity of the Ocean. This small amount of "free" CO_2 in solution is equal to the amount that would be dissolved from the Atmosphere by the Ocean, were it a perfectly neutral solution; it is in fact the quantity of CO_2 which is to be found tabulated in Table 1 for 1 $^0/_{000}$.

It must be pointed out that a Bicarbonate $RHCO_3$ upon being dissolved, first ionizes to produce the same ions as the normal Carbonate. But the concentration of HCO_3' ions is so great in this case, that a further dissociation takes place as follows

$$\left.\begin{aligned} RHCO_3 &\gtrless R\bullet + HCO_3' \\ HCO_3' &\gtrless CO_2 + OH' \end{aligned}\right\}$$

This is in accordance with the well known fact that a solution of a Bicarbonate has a CO_2-pressure far greater than 3 $^0/_{000}$ and consequently evolves CO_2 on agitation, in contact with the air, until the CO_2 partial pressure has sunk to 3 $^0/_{000}$. At this point the solution will then contain HCO_3', OH', $H\bullet$ and $R\bullet$ ions; and the product of the concentrations of $H\bullet$ and OH' will be of course equal to that of water. In other words exactly the same resultant solution will be obtained eventually, by agitating with the air, whether a solution of Carbonate or Bicarbonate (or Hydroxide) be used originally: *i. e.* by starting out with equivalent quantities of Carbonate or Bicarbonate, dissolved in equal quantities of water, at the same temperature of course, and then shaking with the air until equilibrium be reached. In the case of the Carbonate (or Hydroxide), CO_2 will enter the solution; in the case of the Bicarbonate CO_2 will be evolved, until exactly the same point of equilibrium is reached and the solution have a composition in all particulars identical with that obtained by starting out with the Carbonate or Hydroxide. It is apparent then, that it is confusion to speak of Carbonates and Bicarbonates in the case of solutions at all; and to define Alkalinity in the way introduced by Dittmar and Tornöe for sea-water is to misrepresent the facts.

The total Alkalinity of Sea-water, that is the amount of excess Bases, is defined according to modern usage merely as the number of grams OH $^0/_{00}$; just in the same way as Chlorine is expressed as Cl $^0/_{00}$[1]).

[1]) It would be more rational and from some points of view more convenient to use the gram-equivalent $^0/_{00}$ as unit instead of the gram $^0/_{00}$. As however the latter unit is so well established in oceanography it seems, for the present at all events, undesirable to introduce another system of units in speaking of Alkalinity.

The factor for transforming Alkalinity expressed in terms of Dittmar's and Tornöe's definition into grams OH ‰ is $\frac{34}{22.400} = 0.001517$ [1]). Thus the average total Alkalinity of the North Atlantic water in the Irminger Sea, according to Tornöe represented by 26.86 cc CO_2, is $26.86 \times ,001517 = 40.73$ mgms. OH ‰.

The amount of CO_2 found dissolved in sea-water is dependent then, upon four independent variables; namely Pressure, Temperature, Salinity and Alkalinity (the excess of "Base" over "Acid"). The Salinity expressed as Cl ‰ exerts its influence according to the relation tabulated in Table 1; there remains then to be determined the question of the influence of the other three variables

CO_2 dissolves in pure water with formation of Carbonic Acid H_2CO_3, which ionizes according to the relation

$$(H_2CO_3) \gtrless 3 \times 10^7 (H\bullet) \times (HCO_3')$$

There is also the possibility that part of the HCO_3' ions may ionize further

$$HCO_3' \gtrless H\bullet + CO_3''$$

But in the case of all divalent acids the ionization of the second hydrogen atom is always very much less than that of the first. In the case of Carbonic Acid Bodländer [2]) has shown that the second ionization is of the order of magnitude of 20000 times less than that of the first; and as the ionization of the first H• is already exceedingly small (H_2CO_3 is a very weak acid) namely 3×10^{-7} times the amount of H_2CO_3 formed by the combination of CO_2 and water, it may be expected *a priori* that the second ionization is in the case af sea-water also of no account and that consequently no CO_3'' is to be found.

If instead of pure water, however, the CO_2 be dissolved in an alkaline solution, then the hydrogen ions resulting from the ionization of the H_2CO_3 would begin instantly to react with the alkaline hydroxyl ions and would go on reacting to form water.

And in the case of sea-water, instead of pure water (which itself is a solution containing 10^{-7} H• and 10^{-7} OH' ions) there is initially an excess of OH'; and the H• ions resulting from the ionisation of H_2CO_3 therefore react further, as soon as formed, with the excess of OH' to form water. And as the H_2CO_3 continues to go on ionising to form the H• ions necessary, until it has either all disappeared or the OH' has all been transformed into H_2O, it is clear that the

[1]) 34 is the equivalent weight of 2 OH; 22.400 is the volume in cc. occupied at 760 mm and 0° C by the corresponding weight of CO_2, 44 gms.

[2]) *loc. cit.*

reaction involves also a diminution of H_2CO_3 or in other words a diminution of the CO_2 pressure; which is proportional to the H_2CO_3 [1]).

If now Guldberg and Waage's Law be applied to these relations

$$\left.\begin{aligned} CO_2 + H_2O &\rightleftarrows H\bullet + HCO_3' \\ H\bullet + OH' &\rightleftarrows H_2O \end{aligned}\right\} \quad \begin{matrix} \ldots\ldots\ldots\ldots \\ \ldots\ldots\ldots\ldots \end{matrix} \quad \begin{matrix} 1 \\ 2 \end{matrix}$$

there are obtained the following conditions for equilibrium ($k_1 k_2 k_3 \ldots$ representing different Constants; H_2O being present in large quantity is of constant concentration throughout)

$$\left.\begin{aligned} k_1 &= \frac{(CO_2)}{(H\bullet) \times (HCO_3')} \\ (H\bullet) &= \frac{k_2}{(OH')} \end{aligned}\right\} \quad \begin{matrix} \ldots\ldots\ldots\ldots\ldots \\ \ldots\ldots\ldots\ldots\ldots \end{matrix} \quad \begin{matrix} 3 \\ 4 \end{matrix}$$

or
$$k_1 = \frac{(CO_2) \times (OH')}{k_2\,(HCO_3')}$$

or
$$\frac{(CO_2)\,(OH')}{(HCO_3')} = \text{Constant} \quad \ldots\ldots\ldots\ldots\ldots \quad 5$$

where (CO_2) represents the concentration of CO_2 still free after equilibrium has set in and (OH') represents the concentration of the hydroxyl which has taken part in the reaction:

If then

x = total quantity of CO_2 in cc $^0/_{00}$

a = quantity of free CO_2 in cc $^0/_{00}$ at the end,

then the quantity of HCO_3' which has been formed during the reaction is given by

$$a + \frac{HCO_3' \times 44}{61 \times ,001964} = x$$

(0,001964 is the weight of 1 cc. of CO_2 in gms.)

$$(HCO_3') = 0{,}002724\ (x - a) \text{ gms. } ^0/_{00}$$

And if y be the total Alkalinity, expressed as above, in gms. OH' $^0/_{00}$, then the quantity of OH' $^0/_{00}$ which takes part in the reaction, the equilibrium relation of which is expressed in *2*, is

$$(OH') = y$$

On substituting these values, 0,002724 remaining Constant, *5* becomes

$$\frac{ay}{x - a} = \text{Constant}$$

where x, y, a are known. It will be noticed that this equation contains no function of higher power than the first; and the quantity

[1]) It seems to the writer an inevitable conclusion that $^1/_2$ of the CO_2 in the sea must eventually be derivable from the Atmosphere and $^1/_2$ from insoluble carbonates, especially of course, the Ca and Mg carbonates of limestone etc.

$$R{\bullet\bullet}CO_3 + H_2O + CO_2 \rightarrow R{\bullet\bullet} + 2\,HCO_3'.$$

of combined CO_2 is a linear function of the total Alkalinity, if a, and that is p, remain constant.

If on the other hand any appreciable part of the reaction take place according to the relations

$$\left.\begin{array}{c} CO_2 + H_2O \rightleftarrows 2\,H\bullet + CO_3'' \\ H\cdot + OH' \rightleftarrows H_2O \end{array}\right\}$$

then

$$\left.\begin{array}{c} k_1 = \dfrac{(CO_2)}{(H\bullet)^2 \times (CO_3'')} \\ H\bullet = \dfrac{k_2}{(OH\bullet)} \end{array}\right\}$$

and

$$k_1 = \frac{(CO_2) \times (OH')^2}{k_2\,(CO_3'')}$$

or

$$\frac{(CO_2)\,(OH')^2}{(CO_3'')} = \text{Constant} \quad \ldots\ldots\ldots\ldots\ldots \quad 6$$

In this case

$$a + \frac{CO_3'' \times 44}{60 \times 0{,}001964} = x$$

$$(CO_3'') = 0{,}002679\,(x - a)$$

$$(OH')^2 = y^2$$

and *6* takes the form

$$\frac{ay^2}{x - a} = \text{Constant.}$$

The series of experiments now to be described shows that within the limits of the Alkalinity found in the Ocean there is no trace of any appreciable part of the reaction taking place according to the second possibility. For p and t constant and total CO_2 and OH' varying, it is found that *5* gives a satisfactory Constant.

Table 2 contains the numerical details of four series of experiments; in each of which series the temperature and CO_2 pressure (Atmospheric CO_2 pressure) were kept constant, while the Alkalinity and, consequently also the total CO_2, was varied. The results are also given graphically in Fig. 4 where total CO_2 is plotted against OH concentration. It should be stated that the temperature did not always remain quite constant during the set of determinations; but it was observed carefully for each determination and the mean of all taken as the temperature for the series; to which temperature all were subsequently reduced with the help of the fact, later established, that for small temperature changes the amount of CO_2 absorbed is proportional to the absolute temperature. The CO_2 pressure in the air was determined as a rule 2—4 times during the series, depending upon the time taken; the aim was to have a duplicate determination for about every 1—1½ hours. It was found that the pressure did not alter much as a rule; at least so far as the series here recorded are concerned. But alterations of pressure are also more elusive and

more difficult to correct than are temperature alterations. It is believed however, that the means given here are correct to within about 0.05 ‰ at most. A good many series of determinations were

Table 2

	total OH' in grms ‰	total CO_2 cc	free CO_2 cc	$\frac{ay}{x-a}$ = Constant
	2.39	3.65	0.58	.453
t = 3° 22	3.41	4.72	0.58	.478
	19.60	25.50	0.58	.456
p = 3.86 ‰	31.42	40.75	0.58	.453
	46.70	60.03	0.58	.456
Cl = 0.00 ‰	47.18	60.10	0.58	.459
	60.60	77.35	0.58	.458
	7.39	9.40	0.35	.286
t = 11° 51	16.83	21.00	0.35	.285
	30.00	36.77	0.35	.289
	38.04	46.53	0.35	.289
p = 3.63 ‰	40.37	49.40	0.35	.288
	52.96	65.22	0.35	.288
	61.60	75.90	0.35	.285
Cl = 18.22 ‰	78.41	96.50	0.35	.285
	2.00	2.60	0.28	.241
t = 18° 00	14.33	17.38	0.28	.234
	26.02	30.81	0.28	.239
	46.05	55.20	0.28	.235
p = 3.30 ‰	58.53	70.65	0.28	.232
	62.12	73.95	0.28	.236
Cl = 18.22 ‰	78.06	93.55	0.28	.234
t = 26° 46	11.58	13.25	0.25	.224
	29.41	33.90	0.25	.217
p = 3.42 ‰	49.35	57.20	0.25	.216
	64.81	74.42	0.25	.219
Cl = 0.00 ‰				

rejected altogether, because it was thought that the CO_2 pressure had varied too much and that the mean pressure was in consequence not known with sufficient accuracy; in each series rejected it was

found that the Constant expected was recognisable but not well enough defined and that the straight line plotted for the results was unsatisfactorily ragged. There is no doubt that the CO_2 pressure is the most difficult to determine of the measurements which have to be made in this kind of work; and the difficulty must in the writer's

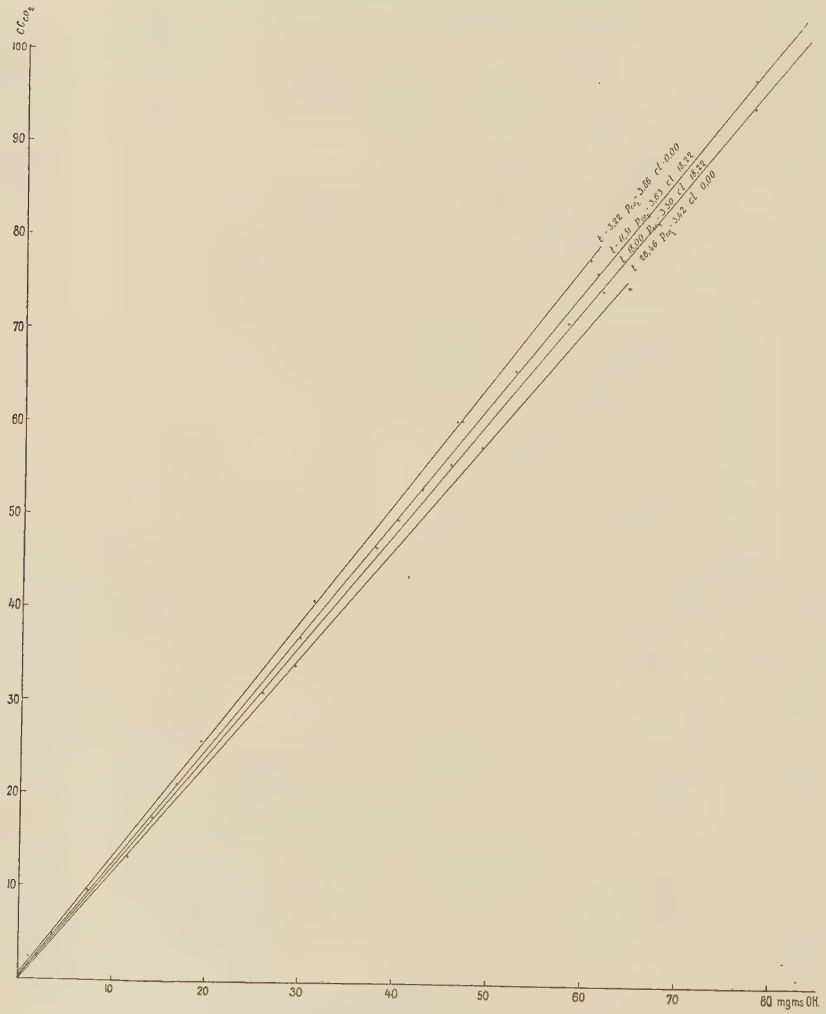

Fig. 4.

opinion, be ascribed chiefly to inevitable variations in the amount of CO_2 in the air of a laboratory (in the open air of cities too) even with very thorough circulation and ventilation. The methods of atmospheric-CO_2 analysis available, are perhaps not capable of giving high precision; but in view of the small total amount of CO_2 and the rapidity of CO_2 variation, greater exactitude is perhaps hardly to be expected.

As was pointed out, it was to be anticipated in the case of such a weak acid as H_2CO_3 and such weak solutions as up to 0.1 gm OH ‰, that the ionisation of the second H• ion must be of quite insignificant amount and this expectation is, as has been found, fully borne out by the perfect linearity of the relationship between HCO_3' (combined CO_2) and OH'[1]). This fortunate circumstance very much simplifies the consideration of the remainder of the problem; namely the effect of variation of CO_2 pressure.

From KROGH's work[2]) it would seem certain that in sea-water CO_2-partial pressures of more than 6 ‰ are altogether exceptional, or perhaps unknown. The present work was therefore limited to a study of the equilibrium relations from 0° to 30°, between CO_2 at varying partial pressures of about 0 to 7 ‰ and sea-water of constant Alkalinity. It had already been found that the effect of Alkalinity is linear; it was only necessary therefore to make use of one Alkalinity in the series of experiments now to be described. That selected was 40.00 mgms OH ‰; which is approximately the Alkalinity of open ocean water[3]) (Tornöe found for the North Atlantic in the Irminger Sea the vatue 26.86 cc CO_2 = 40.73 mgms ‰ OH).

The determinations are contained in Table 3 and the interpolation formula calculated from these observations together with those contained in Table 2, is as follows

$$CO_2 \text{ in cc } ‰ = p\alpha + y[0.9731 - 0.005382\,t + (0.08540 + 0.00113\,t)(p-1) - (0.01587 + 0.000310\,t)(p-1)^2 + 0.001254 + 0.00003455\,t)(p-1)^3]$$

where t = temperature (0°—30° C.)

p = partial pressure of CO_2 (1 — 6.5 ‰)

α = factor depending upon Cl and t and found tabulated in Table 1 for $p = 1$ ‰

y = Alkalinity in mgms OH ‰.

[1]) These lines do not of course pass through the origin, but through points on the vertical axis equal to $p\alpha$ cc above it. It is of interest to point out too, that this linearity is more or less to be recognised upon examination, in HAMBERG's results (see Hamberg Bihang till K. Vet. Akad. Handl. 1884. Band 10 No 13). It is however also apparent that his CO_2 determinations are on the whole either too high or his Alkalinities too low.

[2]) KROGH On the Tension of CO_2 in Natural Waters and especially in the Sea. Meddelelser om Grønland Heft 6/7 Kopenhagen 1904 331—434.

[3]) It will be noticed that the salinity has no distinctly appreciable influence in determining the effect of the Alkalinity upon the amount of CO_2 dissolved; for the formula calculated by using together all the observations made upon solutions of various salinities and distilled water, seems to fit all much about equally well. When it is remembered however, that sea-water contains only about $3^1/_2$ % of salts it is hardly surprising to find that the physical influence upon the water as a solvent, due to the presence of these salts, is very small indeed compared with the enormous chemical effect of the Alkalinity.

The first term $p\alpha$ has, as shown above, always a very small value; which never exceeds 1 cc and may be considered as independent of the Alkalinity.

Table 3

	p	free CO_2	total CO_2 found	total CO_2 calculated
	1.03	.15	44.57	44.47
	1.66	.16	46.94	46.88
t = 2.77	3.21	.47	50.36	50.35
	3.65	.54	50.81	50.77
Cl = 7.14	5.48	.80	52.71	52.80
	5.53	.81	52.65	52.81
OH = 40.00	6.15	.90	53.21	53.42
	6.64	.98	54.12	53.98
	0.73	.08	42.44	42.51
t = 8.06	1.12	.13	43.58	43.61
	1.18	.13	43.95	43.85
Cl = 14.26	3.11	.35	49.17	49.15
	5.37	.61	51.87	51.73
OH = 40.00	6.26	.71	52.62	52.71
	0.77	.09	41.57	41.51
	1.16	.14	43.29	43.16
	1.19	.14	43.23	43.47
	1.63	.19	45.01	45.12
	1.79	.21	45.97	45.81
t = 10.53	2.70	.33	47.91	47.93
	2.79	.33	48.07	48.13
	3.61	.42	49.63	49.51
Cl = 0.00	3.70	.43	49.60	49.63
	3.97	.46	49.90	49.99
	4.12	.48	50.20	50.10
OH = 40.00	4.14	.48	50.09	50.11
	5.31	.62	51.48	51.34
	5.92	.69	51.90	52.03
	6.63	.78	52.97	52.86
	7.02	.82	53.76	53.72
	1.28	.12	42.71	42.60
	1.36	.12	42.64	42.65
t = 14.24	1.98	.18	45.31	45.35
	2.61	.24	47.00	46.93
Cl = 19.46	3.16	.29	48.31	48.05
	3.72	.34	48.84	48.87
	4.53	.42	49.98	49.82
OH = 40.00	4.59	.42	49.97	49.90
	5.22	.48	50.39	50.53
	5.33	.49	50.79	50.72

	p	free CO_2	total CO_2 found	total CO_2 calculated
	1.06	.09	41.35	41.37
t = 15.04	1.45	.11	43.38	43.44
	2.88	.26	47.54	47.43
Cl = 19.46	3 54	.31	48.52	48.51
OH = 40 00	5.01	.45	50.05	50.21
	5.47	.49	50.79	50.69
	1.40	.12	42.06	42.12
t = 20.96	2.47	.19	45.36	45.33
	2.88	.22	46.20	46 29
Cl = 14.36	3.33	.26	47.13	47.14
	3.54	.28	47.64	47.48
	3.72	.29	47.66	47.69
OH = 40.00	4.47	.35	48.51	48.58
	4.86	.38	49.12	49.02
	5.52	.43	49.77	49.79
	5.98	.47	50.58	50.43
	2.23	.17	43.93	43.90
t = 24.18	2.68	.21	44.78	44.72
	3.05	.31	47.52	47.50
Cl = 0.00	4.73	.32	47.66	47.75
	4.88	.38	48.60	48.61
OH = 40.00	5.53	.43	49.47	49.36
t = 28.49	2.02	.12	42.53	42.39
	3.11	.19	45.28	45.31
Cl = 19.48	3.68	.22	46.19	46.35
	5.02	.30	47.94	47.97
OH = 40.00	5.03	.30	48.15	47.97

The data necessary for the calculation of $p\alpha$ have been given already in Table 1; a tabulation of the rest of the expression for the

most useful values of p when $y = 1.000$ is given in Table 4. And as these values are directly proportional to the Alkalinity, all that is required to find the value for Alkalinity different to 1 mgm $^0/_{00}$ is to multiply the numbers in this table by the Alkalinity expressed in mgms $^0/_{00}$.

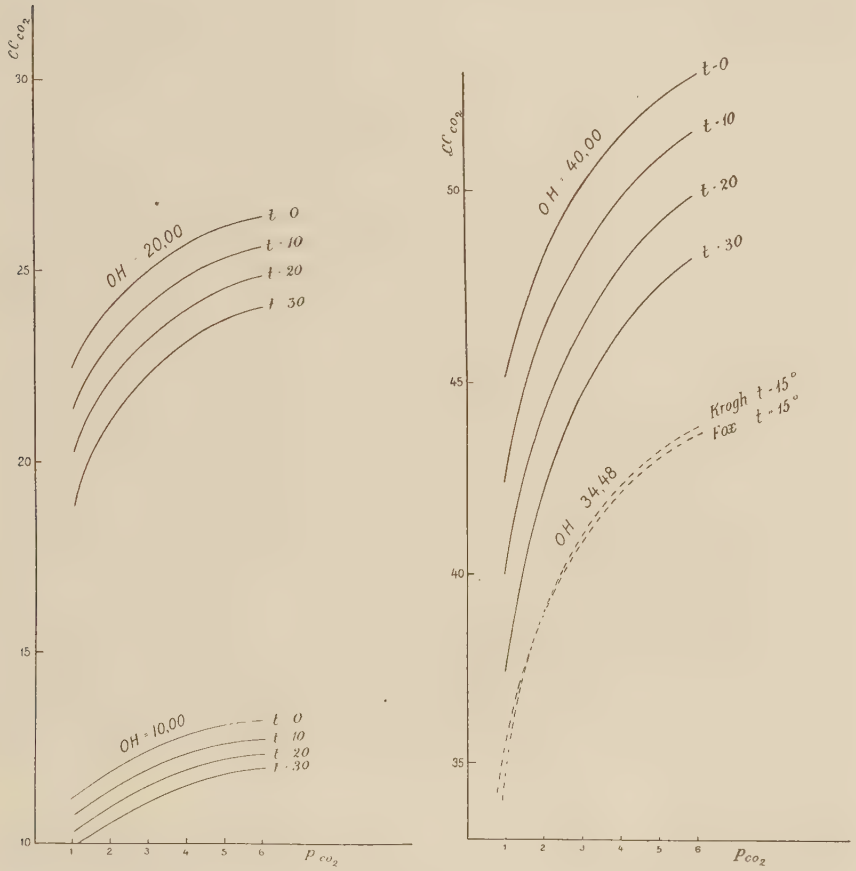

Fig. 5.

In Fig. 5, some results are given graphically for $t = 0°$, 10°, 20°, 30° and Alkalinity 10, 20, 40 mgms $^0/_{00}$. In addition there are given also the values plotted for $t = 15°$ and OH = 34.48 mgms $^0/_{00}$; the values for this temperature and Alkalinity have been determined before by Krogh [1]) and this seems to be the only work previously done with which comparison of the above tables can be made. It will be seen that the agreement between Krogh's one curve and the above table is very satisfactory.

[1]) *loc. cit.* Krogh carried his determinations up to $p = 352$ $^0/_{000}$ but he used only one temperature and one Alkalinity.

Tabl

p	$t=0$	1	2	3	4	5	6	7	8	9	10	11	12	13	14
	1.	1.	1.	1.	1.	1.	1.	1.	1.	1.	1.	1.	1.	1.	1.
1.0	1243	1182	1120	1058	0997	0935	0874	0812	0750	0689	0627	0566	0504	0442	0381
1.5	1673	1617	1562	1506	1451	1395	1340	1284	1229	1173	1118	1062	1007	0951	0896
2.0	2021	1971	1920	1869	1818	1797	1717	1666	1615	1564	1513	1463	1112	1361	1310
2.1	2082	2032	1982	1932	1882	1832	1782	1732	1681	1631	1581	1531	1481	1431	1381
2.2	2140	2091	2042	1993	1943	1894	1845	1795	1746	1697	1647	1598	1549	1500	1450
2.3	2196	2147	2099	2050	2001	1953	1904	1855	1806	1758	1709	1660	1612	1563	1514
2.4	2249	2201	2153	2105	2057	2009	1961	1913	1865	1817	1769	1721	1673	1625	1577
2.5	2300	2252	2205	2157	2110	2063	2015	1968	1920	1873	1826	1778	1731	1683	1636
2.6	2348	2301	2259	2207	2160	2113	2066	2020	1973	1926	1879	1832	1785	1738	1691
2.7	2394	2347	2301	2254	2208	2162	2115	2069	2022	1976	1930	1883	1837	1790	1744
2.8	2437	2391	2346	2300	2254	2208	2162	2116	2070	2024	1978	1932	1887	1841	1795
2.9	2479	2434	2388	2343	2297	2252	2207	2161	2116	2070	2025	1980	1934	1889	1843
3.0	2518	2473	2428	2383	2338	2293	2248	2203	2158	2113	2068	2023	1978	1933	1888
3.1	2556	2512	2467	2422	2378	2333	2289	2244	2199	2155	2110	2066	2021	1976	1932
3.2	2592	2548	2504	2459	2415	2371	2327	2283	2238	2194	2150	2106	2062	2017	1973
3.3	2626	2582	2538	2495	2451	2407	2363	2319	2276	2232	2188	2144	2100	2057	2013
3.4	2658	2615	2571	2528	2484	2441	2397	2354	2310	2267	2223	2180	2136	2093	2049
3.5	2689	2646	2603	2559	2516	2473	2430	2387	2343	2300	2257	2214	2171	2127	2084
3.6	2718	2675	2633	2590	2547	2504	2461	2419	2376	2333	2290	2247	2205	2162	2119
3.7	2746	2704	2661	2618	2576	2533	2491	2448	2405	2363	2320	2278	2235	2192	2150
3.8	2773	2730	2669	2646	2603	2561	2519	2477	2434	2392	2350	2307	2265	2223	2180
3.9	2798	2756	2714	2672	2630	2588	2546	2504	2462	2420	2378	2336	2294	2252	2210
4.0	2822	2780	2739	2697	2655	2613	2572	2530	2488	2447	2405	2363	2322	2280	2238
4.5	2928	2888	2848	2807	2767	2727	2687	2646	2606	2566	2525	2485	2445	2404	2364
5.0	3019	2980	2942	2903	2864	2825	2787	2748	2709	2671	2632	2593	2555	2516	2477
5.5	3105	3068	3032	2995	2958	2922	2885	2849	2812	2775	2739	2702	2666	2629	2592
6.0	3197	3163	3130	3096	3062	3129	2995	2962	2928	2894	2861	2827	2794	2760	2726
6.5	3306	3276	3246	3216	3187	3157	3127	3097	3067	3038	3008	2978	2948	2918	2889

It appears then that the CO_2 found dissolved in sea-water may thus be considered as made up of two parts; a small portion, about 0.5 cc usually, dependent upon pressure temperature and salinity, but independent of the Alkalinity and a larger — in nearly all cases far larger — portion dependent upon the Alkalinity pressure and temperature and independent of the salinity.

In practical Oceanography the total amount of CO_2 the Alkalinity and the temperature of a given sample of sea-water, will usually be determined; and from these it is possible with the help of the above tables to deduce the pressure or tension of the CO_2 and therefore to say whether it is in equilibrium with the Atmosphere or would evolve or absorb CO_2, as the case may be, if in contact with a free atmosphere of specified composition.

4

15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
1.	1.	1.	1.	1.	1.	1.	1.	1.	1.	1.	1.	1.	1.	1.	1.
0319	0258	0196	0134	0073	0112	1.9950	1.9888	$\bar{1}$.9826	$\bar{1}$.9765	$\bar{1}$.9703	$\bar{1}$.9642	1.9580	$\bar{1}$.9518	1.9457	1.9395
0840	0785	0729	0674	0618	0563	0507	0452	0396	0341	0285	0230	0174	0119	0063	0008
1259	1209	1158	1107	1056	1005	0955	0904	0853	0802	0751	0701	0650	0599	0548	0497
1331	1281	1231	1180	1130	1080	1030	0980	0930	0880	0830	0780	0730	0679	0629	0579
1401	1352	1302	1253	1204	1154	1105	1056	1007	0957	0908	0859	0809	0760	0711	0661
1466	1417	1368	1319	1271	1222	1173	1125	1076	1027	0979	0930	0881	0832	0784	0735
1529	1481	1433	1385	1337	1289	1241	1193	1145	1097	1049	1001	0953	0905	0857	0809
1589	1541	1494	1446	1399	1352	1304	1257	1209	1162	1115	1067	1020	0972	0925	0878
1644	1597	1551	1504	1457	1410	1363	1316	1269	1222	1175	1128	1082	1035	0988	0941
1698	1651	1605	1558	1512	1466	1419	1373	1326	1280	1234	1187	1141	1094	1048	1002
1749	1703	1657	1611	1565	1519	1473	1428	1382	1336	1290	1244	1198	1152	1106	1060
1798	1753	1707	1662	1616	1571	1526	1480	1435	1389	1344	1299	1253	1208	1162	1117
1843	1798	1753	1708	1663	1618	1573	1528	1483	1438	1393	1348	1303	1258	1213	1168
1887	1843	1798	1753	1709	1664	1620	1575	1530	1486	1441	1397	1352	1307	1263	1218
1929	1885	1841	1796	1752	1708	1664	1620	1575	1531	1487	1443	1399	1354	1310	1266
1969	1925	1881	1838	1794	1750	1716	1662	1619	1575	1531	1487	1443	1400	1356	1312
2006	1962	1919	1875	1832	1788	1745	1701	1658	1614	1571	1527	1484	1440	1397	1353
2041	1998	1955	1911	1868	1825	1782	1739	1695	1652	1609	1566	1523	1479	1436	1393
2076	2033	1991	1948	1905	1862	1819	1777	1734	1691	1648	1605	1563	1520	1477	1434
2107	2065	2022	1979	1937	1894	1852	1809	1766	1724	1681	1639	1596	1553	1511	1468
2138	2096	2054	2011	1969	1927	1884	1842	1800	1757	1715	1673	1631	1588	1545	1504
2168	2126	2084	2042	2000	1958	1916	1874	1832	1790	1748	1706	1664	1622	1580	1538
2196	2155	2113	2071	2030	1988	1946	1905	1863	1821	1779	1738	1696	1654	1613	1571
2324	2284	2243	2203	2163	2122	2082	2042	2001	1961	1921	1881	1840	1800	1760	1719
2438	2400	2361	2322	2284	2245	2206	2168	2129	2090	2051	2013	1974	1935	1897	1858
2556	2519	2483	2446	2409	2373	2336	2300	2263	2226	2190	2153	2117	2080	2043	2007
2693	2659	2626	2592	2558	2525	2491	2458	2424	2390	2357	2323	2290	2256	2222	2189
2859	2829	2799	2769	2740	2710	2680	2650	2620	2591	2561	2531	2501	2471	2442	2412

Thus supposing that a sample of sea-water were collected with the following properties:

$t = 8°.1$ Cl = 19.5 ‰ OH = 40.52 mgms ‰ CO_2 = 49.02 cc ‰

What is the partial pressure of the CO_2 in this sample? Would it absorb or evolve CO_2 if in contact with a free atmosphere containing 2.95 ‰ CO_2?

$\frac{CO_2}{OH} = \frac{49.02}{40.52} = 1.2095$. On referring to Table 4 it is found that for 8°.1 the factor 1.2095 refers to a CO_2 pressure of roughly 2.85 ‰. From Table 1 it is found that for a water Cl = 19.5 ‰ and t = 8°.1 the amount of „free“ CO_2 held in solution at 2.85 ‰ is $2.85 \times 0.1088 = 0.31$ cc ‰. If this amount of 0.31 cc be now subtracted from the total CO_2, the difference $49.02 - 0.31 = 48.71$ is held in solution by the OH (40.52 mgms ‰). Now $\frac{48.71}{40.52} = 1.2025$; and 1.2025 for t = 8°.1 is

then found from Table 4 to correspond to a CO_2 pressure of 2.71 ‰. That is to say that the water would if in contact with a free atmosphere containing CO_2 = 2.95 ‰ absorb CO_2 from it until its pressure reached 2.95 ‰ also [1]). For p = 2.95 and t = 8°.1 the factor found from Table 4 is 1.2132; that is to say that the water in question would tend to absorb $\frac{1.2132}{1.2025} \times 48.71 - 48.71 = 0.43$ cc ‰ CO_2 from the atmosphere.

In this calculation the pressure of the free CO_2 has been only cursorily estimated as 2.85 and then left further out of account. Practically however it makes no difference whether it be assumed to be 2.5 or 3 ‰ because the total amount of free CO_2 is so very small compared with the rest, and the difference which would be obtained by assuming it to be 3 ‰ instead of 2.5 or *vice-versa* is hardly so much (in the case above considered it is 0.02) as the errors likely to be due to imperfections in the observations upon which the calculations are based.

Krogh [2]) has made determinations of the CO_2-pressure in a number of samples from the neighbourhood of Greenland; unfortunately however he did not determine the Alkalinity simultaneously, though he suggests its importance. If he had determined the Alkalinity it would be possible to deduce the total quantity of CO_2 ‰ from the data given by him; or conversely if the CO_2 had been determined the Alkalinity might have been calculated.

The literature of Oceanography contains very little material as yet, which seems to have been done with the necessary precision and completeness of data, to furnish any useful information upon analysis with the help of the tables above. The writer has examined a great deal of published matter but has been able to find only a very few results which both give data complete enough and which upon scrutiny seem to be reliable enough to furnish deductions of value; deductions have of course been attempted in the past of a similar nature but all who have essayed the attempt seem to have established only very little indeed of general value. The great bulk of material hitherto published is incomplete or the analyses are untrustworthy; in most cases both influences militate against the usefulness of the data. The *Challenger* observations notably, though some of them complete are mostly incomplete. And all or very nearly all are founded on obviously unreliable analyses; in many cases made upon samples very badly preserved, for years.

As an instance of what may be done however, by a critical examination of published data, Table 5 has been worked out from the well known series of observations made upon a few days in July

[1]) This presupposes of course that the atmosphere is so extensive compared with the sea that it would undergo no appreciable change of CO_2 pressure in parting with CO_2 in this way.

[2]) *loc. cit.*

1890 in the Gullmar Fjord by Frk. A. Palmquist[1]). It would seem that this material must be very reliable, as far as it goes; for the values of the partial pressures of CO_2 calculated by means of Table 4 from the data published by Frk. Palmquist, give values which do not differ very widely from the usual CO_2 pressures of the Atmosphere.

The results are tabulated in a form slightly different to that in which they were published originally; that is to say according to the date and depth instead of according to salinity. On all three days the water seems to have been not far from saturated with Nitrogen at all depths. On July 1st however, it seems to have been undersaturated with Oxygen and, in the upper layers, oversaturated with CO_2. Nine or ten days afterwards on July 10—11 conditions seem, as far as can be judged from the somewhat limited material, to have been practically unaltered in the lower layers; while in the upper layers the Oxygen seems to have increased and the CO_2 to have decreased until its partial pressure was actually less than that of the Atmosphere.

It is perhaps not safe under the circumstances to draw far reaching conclusions from what are obviously insufficient data, though as far as it goes seemingly reliable evidence; but the results seem to suggest that plant life was here, under the influence of sunlight, transforming CO_2 into Oxygen. This conclusion might have been strengthened considerably, had there been for July 1st more analyses made upon samples from the surface layers. Knudsen[2]) was able to draw the same sort of conclusion, in a different way, from his work upon the Ingolf expedition.

In passing, attention may be drawn to the fact that a change of CO_2 partial pressure from about 3.5 ‰ (*i. e.* oversaturated sea-water) to about 2.0 ‰ (*i. e.* undersaturated) is accompanied by a decrease in the amount dissolved from 41.5 to 38.3 cc ‰. This unsaturated sea-water of 2 ‰ CO_2 would require actually about 2 cc ‰. or in other words all the CO_2 contained in 7 litres of air, to bring the pressure up to equilibrium with the 3 ‰ of the air. That is to say this sea-water requires something like 21 times as much CO_2 as does the air, to change its CO_2 pressure by the same amount. It has long been known that the sea exerts a strong controlling influence in tending to keep the CO_2 of the air constant; and this seems to be about the order of magnitude of that influence for the conditions prevailing in the Gullmar Fjord in July 1900.

The effect of other Alkalinities and Temperatures upon this influence may be deduced from Table 4. For example it may be seen that the

[1]) Published in O. Pettersson's papers in the Scottish Geographical Magazine for 1894 pp. 300, 526—531, 625—631.

[2]) Knudsen Den Danske Ingolf-Expedition Bd. 1 Heft 1 Kopenhagen 1898.

Table 5

July 1

depth meters	t	Cl	N_2	O_2	CO_2	OH	p_{CO_2} ‰
5	15.4	14.35	11.66	5.99	41.56	34.42	3.6
25	—	—	—	—	—	—	—
35	—	—	—	—	—	—	—
40	—	—	—	—	—	—	—
50	—	—	—	—	—	—	—
55	—	—	—	—	—	—	—
70	5.9	19.61	13.37	4.67	48.09	39.75	2.65
82	—	—	—	—	—	—	—
111	6.0	19.53	13.20	4.82	48.23	39.62	2.8

July 10

depth meters	t	Cl	N_2	O_2	CO_2	OH	p_{CO_2} ‰
5	15.4	13.81	12.40	5.92	38.51	35.59	1.5
	15.2	14.14	11.66	5.64	38.45	34.19	1.95
25	11.8	17.29	12.27	5.87	42.59	38.82	1.8
	11.9	17.49	12.05	5.73	42.20	38.76	1.7
35	—	—	—	—	—	—	—
40	8.9	18.01	12 95	5.55	47 86	38.14	4.5
50	6.1	19.13	13.16	4.78	46.67	39.75	2.05
55	—	—	—	—		—	—
70	—	—	—	—	—	—	—
82	5.8	19.56	12.98	4.75	48.52	39.75	2.9
111	—	—	—	—	—	—	—

July 11

depth meters	t	Cl	N_2	O_2	CO_2	OH	p_{CO_2} ‰
5	15.2	13.95	11.78	6 05	37.72	33.98	1.9
	15.0	14.05	11.79	6.00	38.83	34 48	2.05
25	11.6	17.52	12.17	6.01	44.70	37.82	2.95
35	10.2	17.74	12.68	6.11	42.73	37.76	1.75
40	—	—	—	—	—	—	—
50	—	—	—	—	—	—	—
55	5.8	19.30	12.96	3.97	49.08	39.12	3.9
70	—	—	—	—	—	—	—
82	—	—	—	—	—	—	—
111	—	—	—	—	—	—	—

Alkalinity strongly affects the amount of CO_2 required at a particular temperature, to raise the CO_2 pressure by a given quantity; the amount required to do this is in fact proportional to the Alkalinity. Thus for the very low alkalinity of 10.00 mgms OH ‰, the CO_2

must be raised from 12.0 to 12.5 cc $^0/_{00}$ in order to increase the CO_2 pressure from 2.0 to 3.0; and from 12.5 to 12.8 cc $^0/_{00}$ to increase the pressure further to 4.0 $^0/_{000}$. Table 6 contains data deduced in this way for alkalinities of 10 and 40 at temperatures 0° and 25°; it shows the way in which given additions of CO_2 to sea and atmosphere must be distributed between the two in order that equilibrium between them may be still maintained. Thus it appears that in the case of a sea-water with alkalinity 10 and temperature 0°, a quantity of CO_2 added to the air above it — here for the sake of simplicity supposed to be of equal volume to the sea-water and mixing supposed to be perfect — would distribute itself so that from

Table 6

t	OH	cc CO_2 $^0/_{00}$		cc $^0/_{00}$ increase	
		in air	in water	in air	in water
0	10.00	0.2	12.0	0.1	0.5
		0.3	12.5	0.1	0.3
		0.4	12.8		
25	10.00	0.2	10.7	0.1	0.7
		0.3	11.4	0.1	0.4
		0.4	11.8		
0	40.00	0.2	48.1	0.1	1.9
		0.3	50.0	0.1	1.3
		0.4	51.3		
25	40.00	0.2	42.8	0.1	2.8
		0.3	45.6	0.1	1.6
		0.4	47.2		

$^1/_6$ to $^1/_4$ of it would remain in the air and the remaining $^5/_6$ to $^3/_4$ would dissolve in the water. In the case of a water of alkalinity 40 and temperature 25° the proportion that would dissolve would be between $^{16}/_{17}$ and $^{28}/_{29}$ the residual $^1/_{27}$ to $^1/_{29}$ remaining to augment the CO_2 pressure of the air above it. An inspection of this table shows that increase of temperature and increase of alkalinity both tend to increase the proportion of the CO_2 which dissolves in the water; but that the alkalinity is far more effective in this respect than the temperature, as might be expected also on other grounds.

These numbers express the ratio of concentrations for the air-phase and the water-phase; they would express also the total quantities for the whole Atmosphere and the whole Ocean were they

both of equal volume. As a matter of fact however, the effective volume of the Atmosphere (*i. e.* for CO_2) seems to be about 8 times that of the Ocean[1]). When this is taken into consideration too, it follows that whenever a quantity of CO_2 is added to the Atmosphere (*e. g.* by Volcanic Action) then the total quantity retained by the Atmosphere will be about $^1/_3$ to $^1/_4$ and the remaining $^2/_3$ to $^3/_4$ will be eventually absorbed by the Ocean (OH = 40 $^0/_{00}$). This seems to indicate that the Ocean has considerable, but by no means infinite, power to conserve the constancy of atmospheric CO_2. It must be also remembered however, that an addition of CO_2 to the sea-water will raise its CO_2 pressure and increase its H• concentration accordingly; the water will then be able to dissolve insoluble Carbonates from the sea-bottom etc. at a proportionally faster rate, which will in turn reduce the CO_2 pressure in the water and will thus in the long run indirectly affect that of the Atmosphere. The CO_2 of the Ocean is thus in equilibrium between the Atmosphere at its surface and the insoluble Carbonates of its floor; anything causing a variation of the former must consequently have its counter effect of a corresponding solution or precipitation of insoluble Carbonates, eventually tending to restore the original state of things in the Ocean and Atmosphere[2]). With this reservation, however, the figures given at least serve as a measure of the order of magnitude of the Ocean's capacity to conserve constancy of CO_2 pressure in the Atmosphere above it; a matter which since the publication of ARRHENIUS' work upon the influence of CO_2 in the Atmosphere as an important factor determining terrestrial temperature, has attained considerable Geologic importance[3]). A short resumé of what has been done hitherto in connection with this question will be found in KROGH's paper: "The abnormal CO_2 pressure in the air above Greenland and the general relations between Atmospheric and Oceanic Carbonic Acid". Meddelelser om Grønland Vol. XXVI 409—434.

[1]) According to TH. SCHLOESING Sur la constance de la proportion d'acide carbonique dans l'air. Compt. rend. 90 (1880) 1410 there are 4.7 kgms. CO_2 in the air above and 98 kgms. in the water beneath each sq. metre of the Ocean's surface. On the other hand there is 0.3 cc $^0/_{00}$ in the air and about 50 cc $^0/_{00}$ in the Ocean. The effective volume of the Atmosphere is therefore $\frac{4.7}{98} \times \frac{50}{0.3} = 8$ times that of the Ocean.

[2]) If this line of argument be pressed to its extreme, it would seem to suggest that the CO_2 concentration of the Atmosphere must be in the final analysis, some sort of joint function of the solubility constant of insoluble carbonates and the rate at which CO_2 is supplied to the Atmosphere by volcanic action etc.

[3]) ARRHENIUS On the Influence of CO_2 in the Air upon the Temperature of the ground. Phil. Mag. 1896 pp. 237—276.

It is for some purposes of interest, chiefly in certain Biologic problems, to be able to calculate the concentration of the ions which, it has been seen, are formed by CO_2 in sea-water.

From the deductions made on page 15 it is clear that the concentration of HCO'_3 in grams $^0/_{00}$ is given by $2.724 \times 10^{-3}(x - a)$

where x is the total quantity of CO_2 in cc $^0/_{00}$

a ..... free CO_2 .....

or in gram-equivalents per litre $\frac{0.002724}{61}(x-a) = 4.48 \times 10^{-5}(x-a)$

As $(x - a)$ is seldom more than 50 it is clear that the concentration of HCO_3' will as a rule not exceed about 0.13 gm $^0/_{00}$ or 0.0022 gram equivalents $^0/_{00}$.[1])

It has been pointed out on page 13 that sea-water in equilibrium with the CO_2 of the Atmosphere will just show an exceedingly weak acid reaction due to the H• ions resulting from the ionisation of the small amount of free Carbonic acid; the remainder of the total CO_2 being "neutralised" by the excess of Base over Acid. The ionisation relation of H_2CO_3 is

$$(H\bullet) \times (HCO_3') = 3.04 \times 10^{-7}(H_2CO_3).$$

If the free CO_2 be a cc, the concentration of H_2CO_3 is

$$\frac{0.00196\ a}{44} \text{ gram-equivalents } ^0/_{00};$$

or
$$(H\bullet) \times (HCO_3') = 3.04 \times 10^{-7} \times \frac{.00196\,a}{44}$$
$$= 1.36 \times 10^{-11}\ a$$

And as this free H_2CO_3 ionises into H• and HCO_3' in equal quantities

$$(H\bullet) = \sqrt{1.36 \times 10^{-11} a}.$$

a is practically always 0.2 to 0.5 and (H•) consequently varies from 1.6×10^{-6} to 2.6×10^{-6}. The concentration of H• for distilled water is about 0.4×10^{-7} to 1.5×10^{-7} depending upon the temperature[2]). In other words sea-water reacts *in situ* very nearly neutral; and actually, just slightly more acid than distilled water.

[1]) Though the practice has become well established in Oceanography of defining Salinity and Chlorine in grams $^0/_{00}$ and it would be out of place here to introduce any change of unit, nevertheless in speaking of ionic concentrations it is necessary to introduce the unit of gram-equivalent $^0/_{00}$ and to express quantities in terms of it. The reasons for introducing this change here are that this unit is far more convenient and that all published data of this sort are without exception expressed in this unit.

[2])

$t =$	0°	2°	10°	18°	26°	34°	
(H•) =	0.35	0.39	0.56	0.80	1.09	1.47	$\times 10^{-7}$

Kohlrausch u. Heydweiller Wied. Ann. 53 231 (1894).

It is possible to test this, at least qualitatively by measuring the Elektromotive Force of an electrolytic cell made up of a normal Hydrogen electrode in sea-water, together with a standard Calomel or other electrode[1]). This has been done already by Prof. F. G. Cottrell at the request of Prof. Jacques Loeb and the result is cited by the latter in his work on Dynamik der Lebenserscheinungen "— — — it was found that the concentration of Hydrogen ions was not only not smaller than in pure water but was actually about ten times higher; we may assume therefore that sea-water is normally not only not alkaline but really very nearly neutral".

The writer also did a few such measurements with a cell made up of a standard Calomel elektrode and sometimes a gold sometimes a platinum electrode coated with Palladium charged with hydrogen, and dipping into sea-water. The results, which are very difficult to obtain constant, were always in every case more than 10^{-7} and less than 10^{-5} for the concentration of H•; in other words in complete accord with Cottrell's observation and the requirements of theory.

Of late years it has been shown by various workers[2]) that blood is a fluid which shows a very slightly acid reaction *in situ*, with H• concentration very little more than that of pure water. It is clear therefore that the blood of animals, including fish, (and presumably the other fluids of the body) also reacts in just the same way as sea-water and is in fact neutral to it. This is a physiological fact of considerable importance already pointed out by Loeb. And upon reflection this, is on the whole, just what might be expected when it is remembered that CO_2 of low pressure 3 ‰, is practically all pervading and constant over the earth; in the long run therefore, all masses of water and fluids, including those in the bodies of animals, which behave for the most part as aqueous solutions, must eventually come into equilibrium with it. Such solutions must continue absorbing CO_2 until saturated with free CO_2 at the pressure and temperature prevailing. Then equilibrium having been reached the CO_2 pressure of the solution will be 3 ‰, indicative of the presence of the corresponding amount of free CO_2 of pressure equal to that of the atmosphere. In other words the solution is then equivalent to a very weak solution of H_2CO_3, of strength proportional to the amount of free CO_2; and it consequently reacts very slightly more acid than pure water. It is to be expected that all solutions found in Nature whether of biologic or geologic origin immediately, must eventually show the same weak acid reaction due to the effect of

[1]) *e. g.* see Ostwald-Luther *cit.* or Lehfeldt *cit.*

[2]) Höber, Pflügers Arch. Bd. 81 (1900) 56; *ibid* Bd. 99 (1903) 572. G. Farkas *ibid* Bd. 98 (1903) 551.

the all pervading presence over the earth of CO_2 of low pressure; that is of course, unless the liquid instead of being neutral or alkaline initially, is already acid from some other entirely different cause.

In conclusion the writer desires here to record his indebtedness to Mr Gustav Johnson of the Pharmacological Institute in the University of Christiania for his invaluable help in making many of the measurements given in this paper.

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